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Anisotropic superconducting properties of MgB_2 single crystals probed by in-plane electrical transport measurements

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We report on the study of the electronic anisotropy of the MgB_2 superconductor using the in-plane resistivity measurements in the magnetic field applied perpendicular and parallel to Mg and B planes of MgB_2 single crystals. The results show the temperature dependent anisotropy of the upper critical field with the anisotropy ratio $\gamma = H_{c2\parallel}/H_{c2\perp}$ increasing from 2.2 close to T_c up to about 3 below 30 K. Our estimation of the in-plane and out-of-plane coherence length of about $\xi_{ab}(0) = 68$ Å and $\xi_c(0) = 23$ Å and the electronic mean-free path $l_{ab} = 240$ Å and $l_c = 60$ Å, respectively, indicates MgB_2 single crystal approaches the clean limit type-II superconductor.

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The superconductivity at about 39 K in magnesium diboride[1] has stimulated considerable interest in the study of various properties of this compound. Observation of the boron isotope effect[2] as well as band structure calculations[3] indicate phonon-mediated superconductivity in MgB_2. Transport and magnetization measurements of the upper critical field[4–8] and critical current density[9,10] of MgB_2 revealed properties typical for a type-II superconductor. Since the crystal structure of MgB_2 consists of alternating Mg and B sheets, the electronic anisotropy of this material may be expected. Clear signs of the anisotropic nature of MgB_2 has been demonstrated from measurements performed on thin films,[11,12] aligned crystallites,[13] and fine powder[14] samples. However, results obtained by various groups give very different estimations of H_{c2} anisotropy ratio ranging from $\gamma = 1.7-2$ obtained for thin films[11,12] and aligned crystallites[13] up to $\gamma = 6-9$ for randomly oriented powder samples.[14]

Recently Lee *et al.* reported on the growth of submillimeter MgB_2 single crystals under high pressure in the Mg-B-N system.[15] The availability of such crystals opens a nice opportunity for direct probe of anisotropic behavior of the MgB_2 superconductor, and from resistivity measurements performed in Ref. 15 the upper critical field anisotropy ratio of about 2.7 was estimated.[16] Here we present results of the detailed study of the in-plane transport properties of MgB_2 single crystals in magnetic field up to 6 T applied perpendicular to Mg and B planes ($H_\perp$) and up to 16 T in parallel field orientation ($H_\parallel$). The obtained results allow one to determine the upper critical fields and, thus, to get information about superconducting coherence lengths and superconducting state anisotropy.

Magnesium diboride single crystals have been grown in the quasiternary Mg-MgB_2-BN system at high pressure and temperature of 4–6 GPa and 1400–1700 °C, respectively. The MgB_2 precursor was prepared from magnesium powder (99.9% Rare Metallic Co.) and amorphous boron (97% Hermann C. Starck). Single crystal growth was performed in BN crucibles in the presence of longitudinal temperature gradient of about 200 °C/cm in a cubic-anvil press (TRY Engineering). In optimal conditions shiny gold-colored single crystals of size up to 0.7 mm were grown. Several platelike single crystals of size of about $0.5 \times 0.1 \times 0.05$ mm^3 have been chosen for our study. The in-plane transport measurements have been performed in a usual four probes linear geometry with transport current directed along Mg and B planes. Electrical contacts were made using gold or silver paste without subsequent heat treatment. Contact resistance was around 1 Ω for current contacts and slightly higher (about 3–5 Ω) for potential ones. To measure current-voltage response, we used usual low frequency (17 Hz) lock-in ac technique with excitation current in the range 0.2–2.0 mA and voltage resolution of about 0.3 nV. Magnetic fields up to 9 T were generated by superconducting solenoid, while measurements in high fields up to 16 T were performed in a pulsed magnet. For measurements inside superconducting solenoid the samples were mounted in a rotatable sample holder with an angular resolution of 0.05°, allowing for accurate single crystal alignment with respect to magnetic field. In pulsed magnetic field experiments, accuracy of field alignment along Mg and B planes is estimated to be within 2°–3°.

In Fig. 1, we present zero-field temperature dependence of the resistance for several MgB_2 single crystals. The inset in Fig. 1 is an enlarged view of the resistivity data near T_c. The results for three different samples demonstrate remarkable reproducibility giving a proof of high quality of our single

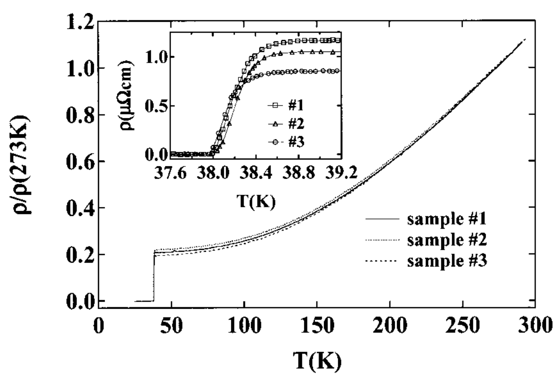

FIG. 1. Normalized zero-field temperature dependence of the in-plane resistivity for three different MgB_2 single crystals measured at current 0.5 mA. Inset: Zero-field resistive superconducting transitions for the same crystals.

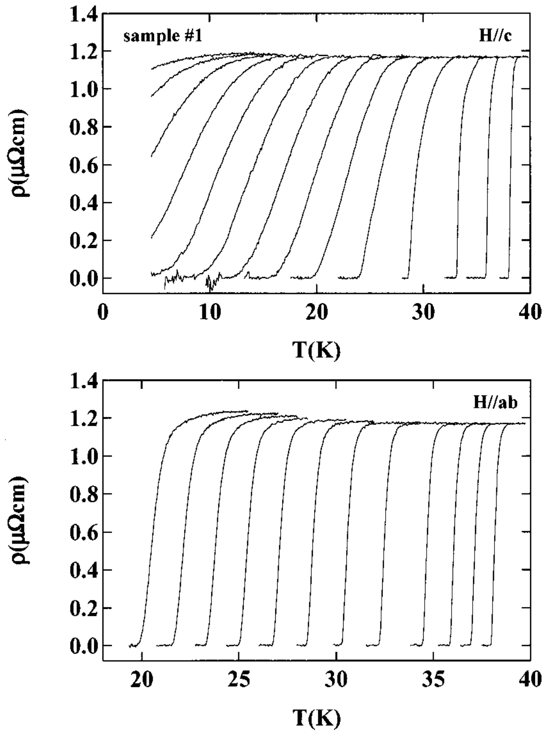

FIG. 2. Upper panel: Superconducting transitions at various magnetic fields of (from right to left) 0, 0.2, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, and 6 T applied perpendicular to Mg and B planes. Lower panel: Superconducting transitions in parallel fields of (from right to left) 0, 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, and 9 T. In both field orientations $I = 0.5$ mA and its direction is perpendicular to the magnetic field. Different transition temperatures for a given applied field demonstrate the upper critical field anisotropy of MgB_2 single crystal.

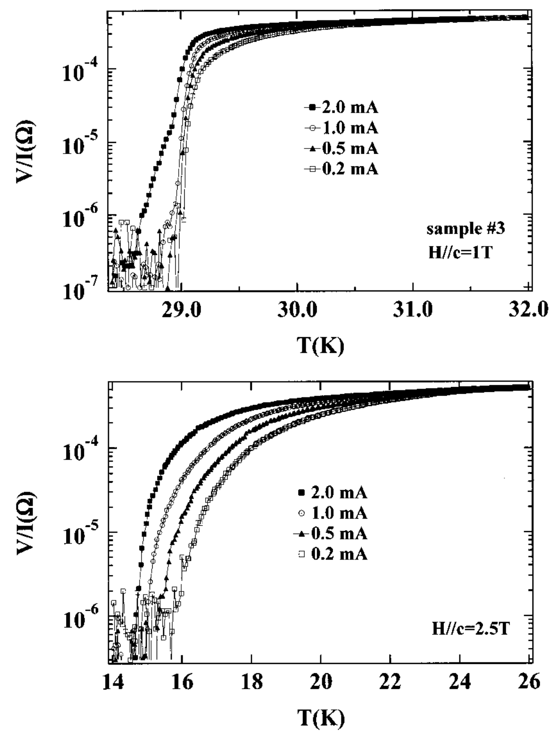

FIG. 3. Temperature dependence of the voltage response at various currents in magnetic field of 1 T (upper panel) and 2.5 T (lower panel) applied perpendicular to Mg and B planes.

crystals. In particular, all samples show sharp superconducting transitions at T_c, defined as the resistivity onset with criterion of 2% of the full resistivity drop, around 38.5–38.6 K with a transition width $\Delta T(10\text{–}90\,\%) < 0.3$ K. Just above the superconducting transition, at $T = 40$ K, we estimate $\rho = 1 \pm 0.15\ \mu\Omega$ cm. Some scattering in the absolute values for the resistivity of different samples is believed to be due to the uncertainty in contact geometry resulting from small crystal size. In the normal state $\rho(T)$ dependence is well fitted to a power law T^{α} with $2.7 < \alpha < 2.8$ at $T < 200$ K, which is similar to previously reported results obtained on bulk sintered polycrystalline samples.[5,7] Also, for all three single crystals we found close values of residual resistivity ratio, $\mathrm{RRR} = \rho(273\ \mathrm{K})/\rho(40\ \mathrm{K}) = 4.9 \pm 0.3$.

The characteristic results of our experiment are shown in Fig. 2. Plotted are resistive superconducting transitions for sample 1 at various magnetic fields up to 6 T for H perpendicular to Mg and B planes (upper panel) and up to 9 T in $H \| ab$ orientation (lower panel). In both orientations transport current direction is perpendicular to magnetic field. Before we start to describe the anisotropic properties of MgB_2 single crystal, let us briefly consider peculiar voltage noise appearing in $H \| c$ field orientation in the low temperature part of the superconducting transition at $T < 15$ K (see upper panel of Fig. 2). Although the maximal value of noise level was found to decrease at smaller excitation currents (not shown), this noisy voltage response was clearly seen at the lowest value of transport current $I = 0.2$ mA ($J \approx 4$ A/cm^2) used in our study. Very similar behavior was also found in the measurements on samples 2 and 3, thus, indicating its intrinsic origin, probably related to the weak pinning properties of MgB_2 single crystal. However, for the context of the present paper, we note that this voltage noise does not affect our observation of anisotropic superconducting properties and defer its further discussion.

From different transition temperatures at a given value of magnetic field, the anisotropic behavior of MgB_2 single crystal is clearly seen in Fig. 2. In particular, increasing $H \| c$ results in a much more rapid T_c decrease compared to $H \| ab$ field geometry. At $H_\perp = 6$ T the superconducting transition is almost completely suppressed above $T = 4.2$ K, while in parallel field of the same magnitude it was found around 25 K. Also, with the increase of magnetic field the structure of superconducting transition itself changes in a very different way in two field orientations. For $H \| ab$ the effect of magnetic field is to shift the transition to lower temperatures with a relatively small ΔT increase. On the contrary, in $H \| c$ orientation, at fields of about 1–1.5 T we found a drastic change of the shape of the superconducting transition. Figure 3 illustrates this observation in more detail. Plotted are voltage response vs temperature for sample 3 taken at various currents at $H = 1$ T (upper panel) and $H = 2.5$ T (lower panel). At $H = 1$ T the superconducting transition is extremely sharp at low currents, while at $H = 2.5$ T the voltage response displays a more gradual behavior with temperature. This observation resembles transformation of the superconducting tran-

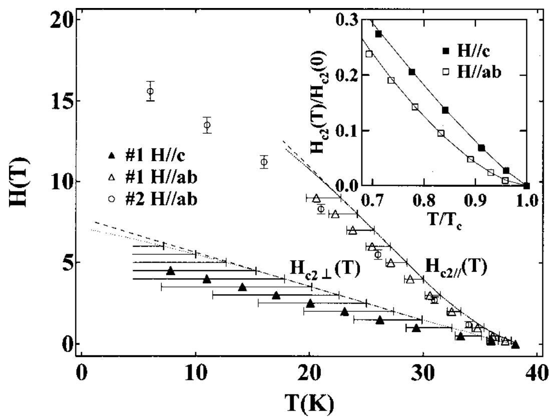

FIG. 4. Magnetic phase diagram of MgB_2 single crystal deduced from the in-plane temperature-dependent (sample 1) and field-dependent (sample 2) resistivity data as described in text. For sample 1 resistivity onset and transition endpoint are vertical bars and symbols are midpoints of the transition as a function of temperature. For sample 2 horizontal bars and symbols show resistivity onset, completion, and transition midpoint as a function of magnetic field, respectively. For both samples the solid lines demonstrate transition width. The dotted lines are guides for the eye and represent temperature dependence of parallel ($H_{c2\parallel}$) and perpendicular ($H_{c2\perp}$) upper critical field for sample 1. The dashed lines represent a linear fit to $H_{c2\parallel}(T)$ and $H_{c2\perp}(T)$ at intermediate temperatures. Inset: $H_{c2}(T)/H_{c2}(0)$ vs T/T_c near T_c for magnetic field parallel and perpendicular to Mg and B sheets ($T_c=38.5$ K, $H_{c2\parallel}(0)=21$ T, $H_{c2\perp}(0)=7.3$ T). Lines represent fit to Eq. (1).

sition near the critical point in the melting line of "clean" $YBa_2Cu_3O_{7-\delta}$ single crystals, where the sharp resistance step associated with the flux line lattice melting below the critical point was replaced by a smooth continuous transition at higher fields.[17] From both panels in Fig. 3 one can also see strongly non-Ohmic behavior developing in the entire temperature region below T_c. We rule out the possibility that this nonlinearity may be due to simple thermal effects since in measurements of zero-field transitions linear voltage response was found in the same range of excitation currents. We note that the non-Ohmic behavior found in MgB_2 single crystals is in striking contrast to the linear voltage response observed in the broad region of the vortex-liquid state above the melting transition in $YBa_2Cu_3O_{7-\delta}$ single crystals.[18,19]

Now we discuss the magnetic phase diagram of MgB_2 single crystal deduced from our in-plane transport measurements (see Fig. 4). Since for sample 1 superconducting transition was measured by sweeping temperature at fixed magnetic fields, for each field three data points are shown as a function of temperature: resistivity onset, transition midpoint, and temperature of vanishing resistivity. On the other hand, for sample 2, measurements have been performed at fixed temperatures in a pulsed field, and the same three points on the superconducting transition are shown in dependence on field. As mentioned above, we associate resistivity onset with the upper critical field, $H_{c2}(T)$. The data for both single crystals demonstrate relatively close agreement. Slightly lower values of the upper critical fields for sample 2 may be due to possible field misalignment from the *ab* planes in pulsed magnetic field experiment.[20] For both field orientations $H_{c2}(T)$ dependence shows distinct positive curvature extending from T_c down to approximately 30 K. Similar positive curvature of $H_{c2}(T)$ dependence was recently observed on dense MgB_2 wires[7] as well as sintered polycrystalline samples.[5,8] With the further decrease of temperature $H_{c2\parallel}(T)$ as well as $H_{c2\perp}(T)$ dependence display linear increase and below 15–20 K start to saturate. The upper critical field anisotropy ratio, $\gamma=H_{c2\parallel}/H_{c2\perp}=(m_c/m_{ab})^{0.5}$, calculated for sample 1 at different temperatures, shows temperature dependence increasing from $\gamma=2.2$ close to T_c up to $\gamma\approx3$ at $T=30$ K. At lower temperatures γ remains nearly unchanged. The obtained value of the electronic anisotropy $\gamma\approx3$ places the MgB_2 compound in between strongly anisotropic high-T_c superconductors with anisotropy ratio ranging from $\gamma=5-7$ for optimally doped $YBa_2Cu_3O_{7-\delta}$ up to $\gamma=50-200$ for $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Ref. 21) and slightly anisotropic ($\gamma=1-1.15$) other layered boride superconductor $R$$Ni_2B_2C$ ($R=$Y, Lu) with crystal structure composed of alternating RC and Ni_2B_2 sheets.[22]

From the available data for sample 1 we estimate $H_{c2\perp}(0)=7.0-7.5$ T and $H_{c2\parallel}(0)=\gamma H_{c2\perp}(0)=21-22$ T. According to the relations for anisotropic superconductors $H_{c2\perp}(T)=\phi_0/(2\pi\xi_{ab}{}^2)$, where ϕ_0 is the flux quantum and $\gamma=H_{c2\parallel}(0)/H_{c2\perp}(0)=\xi_{ab}(0)/\xi_c(0)$, this corresponds to the in-plane and out-of-plane coherence length $\xi_{ab}(0)\approx68$ Å and $\xi_c(0)\approx23$ Å, respectively. Using normal state resistivity measurements of $\rho(40\text{ K})=1\ \mu\Omega$ cm, the in-plane Fermi velocity of 4.9×10^7 cm/s (Ref. 3), and a carrier density of $6.7\times10^{22}\ e/\text{cm}^3$ for two free electrons per unit cell, we evaluate the in-plane electronic mean-free path of about 240 Å near T_c. The out-of-plane resistivity for MgB_2 single crystals is about four times higher compared to the in-plane one.[23] Given the out-of-plane Fermi velocity of 4.76×10^7 cm/s (Ref. 3) we get the out-of-plane mean-free path of about 60 Å close to T_c. Thus, comparable values of coherence length and electronic mean-free path indicate our MgB_2 single crystal as approaching clean limit type-II superconductor.

Finally, we discuss peculiar upward curvature in $H_{c2}(T)$ dependence observed for MgB_2 single crystals near T_c. Similar positive curvature in $H_{c2}(T)$ has been previously reported for intermetallic borocarbides.[22,24,25] It was successfully described within the effective two-band model for type-II superconductors in the clean limit.[24] As mentioned above, MgB_2 single crystal is also close to the clean limit. On the other hand, some differences between MgB_2 and borocarbides should be noted. In $R$$Ni_2B_2C$ ($R=$Y, Lu) compounds $H_{c2}(T)$ dependence displays the same positive curvature for both parallel and perpendicular magnetic field orientations, and the out-of-plane anisotropy of H_{c2} does not depend on temperature.[22,25] In striking contrast, in MgB_2 the upward curvature in $H_{c2}(T)$ is much more pronounced in parallel magnetic field orientation compared to perpendicular (see inset in Fig. 4). In the temperature range above 0.7 T/T_c $H_{c2}(T)$ dependence for both field orientations may be well fitted by the expression

$$H_{c2}(T)/H_{c2}(0)=A(1-T/T_c)^{\alpha}, \qquad (1)$$

with very different fitting parameters A and α: $A=1.225$, $\alpha=1.185$ and $A=1.62$, $\alpha=1.59$ for $H\|c$ and $H\|ab$, respectively. Furthermore, due to the different temperature dependence of $H_{c2\|}$ and $H_{c2\perp}$ the upper critical field anisotropy shows remarkable temperature dependence increasing from 2.2 close to T_c up to about 3 below 30 K. Also, it is worth mentioning that to the best of our knowledge exponent $\alpha=1.59$ obtained for $H\|ab$ geometry is one of the highest values so far experimentally found for any superconductor. From a theoretical point of view such large exponents exceeding 1.5 have been predicted for narrow-band systems with local attractive interactions.[26] However, a negative curvature of $H_{c2}(T)$ dependence clearly observed in MgB_2 at $T<0.4-0.5T_c$ (see Fig. 4) is different from the low-temperature behavior expected for superconductors with local pairing.[26] This brief discussion clearly demonstrates the need for more work on magnetic phase diagram of MgB_2 close to T_c including detailed theoretical study of $H_{c2}(T)$ as well as further experiments on MgB_2 single crystals, e.g., measurements of $H_{c2}(T)$ by various methods.

In summary, we have used the in-plane transport measurements in magnetic field applied perpendicular and parallel to Mg and B sheets of MgB_2 single crystals to determine the upper critical field anisotropy of this recently discovered superconductor. The results indicate moderate value of the upper critical field anisotropy ratio that is nearly temperature independent at about 3.0 below 30 K and monotonously decreases to $\gamma=2.2$ approaching T_c.

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